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(54) Production of Hydroquinone.

(57) A process for making hydroquinone from phenol wherein phenol is oxidised in the presence of a copper catalyst to p-benzoquinone and the p-benzoquinone is directly hydrogenated without additional catalyst to hydroquinone.

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PRODUCTION OF HYDROQUINONE

This invention relates to the production of hydroquinone.

It is known that phenol can be oxidised to p-benzoquinone in the presence of copper catalysts; see for example US-PS 3,987,068. Improvements to these copper-catalyzed oxidations of phenol to p-benzoquinone have been disclosed and claimed in EP-A 0070665 and European Patent Application No. 83300210.8.

Heretofore, p-benzoquinone has been converted to hydroquinone by the use of various catalysts. Thus, for example, Sabatier passed quinone vapours mixed with hydrogen over a reduced copper catalyst (e.g., a heterogeneous vapour-phase system) to obtain hydroquinone (Comptes rendus Ac. Sc. vol. 146, p. 457, 1908 and vol. 172 p. 733, 1921), but in this process the catalyst has a very limited life. R. Cornubert and J. Phelisse, Compt. Rend. 229, 460 (1949) disclose use of Raney nickel to convert quinone to hydroquinone. US-PS 2,495,521 discloses nickel, cobalt, or copper-catalyzed heterogeneous vapour phase hydrogenation of benzoquinone in the presence of steam. Popova et al., Chem. Abs. 53,275 (1959) disclose hydrogenation of benzoquinone with nickel, platinum and palladium - calcium carbonate. M. Calvin, J. Am. Chem Soc. 61 2230 (1939) discloses use of a copper-quinoline complex derived from cuprous acetate to promote hydrogenation of purified quinone, but this process is limited in

that, at most, only one-half mole of hydrogen is taken up per mole of the Copper I - quinoline complex and thus the hydrogenation is very inefficient and perhaps not catalytic. Also of interest is the disclosure of Yananaka et al., Bull. Inst. Phys. Chem. Research (Tokyo) 14, 31 1935 which reduces quinones to oxy compounds with copper and Al_2O_3-promoted nickel.

We have now found that a good yield of hydroquinone is readily obtained when the p-benzoquinone in a reaction mass obtained by oxidation of phenol with a copper catalyst is hydrogenated directly, i.e., without isolation, and without any additional catalyst. It is quite obvious that such a "one-pot" process provides a highly efficient means to obtain hydroquinone which is a commercial chemical much used in the photographic industry and as an inhibitor used in the stabilization of rubber compounds.

Thus, the present invention provides a process for making hydroquinone from phenol by oxidation of phenol to p-benzoquinone and conversion of p-benzoquinone to hydroquinone, characterised in that phenol is oxidised in the presence of a copper catalyst to p-benzoquinone and the p-benzoquinone is directly hydrogenated without additional catalyst to hydroquinone.

The oxidation of phenol to p-benzoquinone with a copper catalyst is, as indicated, well known in the art and any of such processes may be used. Preferably, a process such as that disclosed in US-PS 3,987,068 will be used. Most preferably, the hydrogenation step of this invention will be used with the processes disclosed in (a) EP-A 0070665

where a divalent copper catalyst promoted with an alkali metal is used (molar ratio of base to copper being no greater than about 2.0) and may also be further enhanced with water in an amount less than about 10% by volume of the reaction solution, and (b) European Patent Application No. 83300210.8 where a monovalent copper catalyst promoted with water is used (preferably 1 to 4 moles of water per mole of phenol).

The hydrogenation step in the process will be carried out in a homogeneous, liquid phase simply by first removing oxygen from the system and then pressuring in hydrogen to a pressure of 34 to 345 bar gauge, preferably 69 to 207 bar gauge (about 500 to about 5000 psig, preferably about 1000 to about 3000 psig) and effecting the hydrogenation at a temperature from about 100° to about 200°C, preferably from about 125° to about 175°C.

In order to further exemplify the process, the following Examples are given:

Example 1

500 mmole of phenol are oxidised in 350 ml of acetonitrile containing 35 mmole of $CuCl_2$. An oxygen-containing gas (39% O_2, 61% N_2) is continuously sparged through the mixture at 65°C and 52 bar (750 psi) at 500 ml/hr. After four hours the reaction mixture contains four mmole of phenol, 263 mmole of benzoquinone and six mmole of p-chlorophenol (99% conv., 53% selectivity). The oxygen is flushed from the system and hydrogen gas is admitted to a pressure

of 207 bar (3,000 psi). The mixture is heated for fifteen hours at 175°C to give 135 mmoles of hydroquinone, 2 mmoles of unreacted p-benzoquinone, 17 mmoles of catechol, 6 mmoles of p-chlorophenol, 17 mmoles of phenol and a large amount of quinhydrone (a 1:1 complex of hydroquinone and p-benzoquinone). Yield calculations are difficult because of the low accuracy of the quinhydrone analysis, but a yield of up to about 71% is believed to be achieved.

Example 2

In an experiment similar to Example 1, except that the $CuCl_2$ catalyst is promoted with LiOH (one mole per mole of $CuCl_2$), selectivity to p-benzoquinone is about 70% at 99% conversion. The reaction mixture is hydrogenated by pressurizing 138 bar (2000 psi) of hydrogen on it at 175°C to give a yield of hydroquinone about the same as in Example 1.

Example 3

Similar results are obtained when the process of Example 1 is carried out with a CuCl catalyst promoted with 500 mmole of water.

CLAIMS

1. A process for making hydroquinone from phenol by oxidation of phenol to p-benzoquinone and conversion of p-benzoquinone to hydroquinone, characterised in that phenol is oxidised in the presence of a copper catalyst to p-benzoquinone and the p-benzoquinone is directly hydrogenated without additional catalyst to hydroquinone.

2. A process as claimed in claim 1, wherein the copper catalyst used in the oxidation of phenol is divalent and is promoted with an alkali metal.

3. A process as claimed in claim 1, wherein the copper catalyst used in the oxidation of phenol is a monovalent copper catalyst promoted with water.

4. A process as claimed in any of claims 1 to 3, wherein the hydrogenation is carried out under a hydrogen pressure of from 34 to 345 bar gauge and at a temperature of from 100 to 200°C.

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(54) **Production of Hydroquinone.**

(57) A process for making hydroquinone from phenol wherein phenol is oxidised in the presence of a copper catalyst to p-benzoquinone and the p-benzoquinone is directly hydrogenated without additional catalyst to hydroquinone.

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EUROPEAN SEARCH REPORT

0093540

Application number

EP 83 30 2225

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
A	TETRAHEDRON LETTERS, no. 10, 1977, pages 821-824, Pergamon Press, GB; D. BONDON et al.: "Nouvelle méthode d'aromatisation de cyclohexenones contenues dans des systèmes polycycliques" * Page 821, paragraph 3; page 823, table I *	1	C 07 C 37/07 C 07 C 39/08

A	US-A-3 794 668 (THOMAS H. LARKINS) * Column 5, line 29 - column 6, line 12 and lines 26-52 *	1	

A	US-A-3 859 365 (DAVID A. YOUNG) * Column 3, line 20 - column 4, line 16 *	1	TECHNICAL FIELDS SEARCHED (Int. Cl. 3)

A	US-A-3 213 114 (HENRY G. BRAXTON) * Column 9, line 42 - column 10, line 15; column 4, line 42 *	1	C 07 C 37/00 C 07 C 39/00

D,A	JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 61, no. 8, 5th August 1939, pages 2230-2234, US; M. CALVIN: "Homogeneous catalytic hydrogenation" * Page 2234, summary *	1	
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	13-06-1984	SUTER M.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document

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0093540
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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
D,X	US-A-3 987 068 (E.L. REILLY) * Column 9, lines 15-35 * ---	1	
D,P	EP-A-0 070 665 (SUN TECH, INC.) * Page 10, claim 1 * ---	1	
D,E	EP-A-0 084 448 (SUN TECH, INC.) * Page 10, claim 1 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)

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X : particularly relevant if taken alone
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A : technological background
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& : member of the same patent family, corresponding document

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